Macromolecules 1992, *25*, 3942-3947

Polymer Topology and Diffusion: A Comparison of Diffusion in Linear and Cyclic Macromolecules

S. F. Tead* and E. J. Kramer

Department of Materials Science and Engineering, Bard Hall, Cornell University, Ithaca, New York 14853-1501

G. Hadziioannou

Department of Chemistry, Groningen University, Nijenborgh 16, 9747 AG Groningen, The Netherlands

M. Antonietti and H. Sillescu

Institut für Physikalische Chemie, University of Mainz, Mainz, West Germany

P. Lutz and C. Strazielle

Centre de Research de Macromolecules, CNRS, Strasbourg, France

Received December 5, 1991; Revised Manuscript Received March 25, 1992

ABSTRACT: Diffusion experiments using polystyrene (PS) molecules of three different topologies, linear, ring, and microgel, were performed. Tracer diffusion of linear PS in ring matrices was found to be nearly identical to that in linear matrices, a surprising result in view of current theories for matrix-dependent tracer diffusion. The first unambiguous data showing a lower limit for the tracer diffusion coefficient D^* of ring molecules in linear PS of high molecular weight are presented. These data support the hypothesis that ring-shaped molecules can undergo a form of reptation. The tracer diffusion coefficient of ring molecules of molecular weight M in intramolecularly cross-linked PS (microgel) matrices was found to scale as $M^{-4.5\pm0.2}$, a higher M dependence than has been observed for rings diffusing in linear matrices.

Introduction

Diffusion in Systems of Linear Polymers. The recent development of methods to measure diffusion in polymer melts has stimulated the development of models for polymer motion in the melt. The most successful treatment of the diffusion of a theoretical test or tracer chain (experimentally approximated by labeled polymers in low concentration) in the melt has been the reptation model of de Gennes,[1,2] Doi and Edwards,[3] and Graessley.[4,5] The basis of the reptation model is the curvilinear (snakelike) motion of the tracer chain along its own contour. Such motion is necessitated by the presence of the constraints (due to neighboring chains) on the motion of the tracer chain perpendicular to its own contour. The diffusion coefficient for linear tracer chains of molecular weight M, diffusing in a host matrix of linear chains with molecular weight P (where both M and P are greater than the critical entanglement molecular weight M_c), is then

$$D_R = D_0 M^{-2} \tag{1}$$

where D_0 is related to the parameters M_0, the monomer molecular weight, M_e, the entanglement molecular weight, ζ_0, the monomeric friction coefficient, and k_B, the Boltzmann constant, via[4]

$$D_0 = (4/15) M_0 M_e k_B T/\zeta_0 \tag{2}$$

The motion of the matrix chains is disregarded in the reptation model, and therefore D_R is independent of P. This model has served well in melts of linear chains where P is much greater than M,[6,7] since in such a case the motion of the matrix chains is negligible during the time it takes the M chains to move distances on the order of the radius of gyration. In addition, the dependence of the diffusion coefficient on the concentration of long P chains in the melt (which affects its glass transition temperature and M_e) is also predicted well by eqs 1 and 2.[8]

For systems in which P is less than M, the constraint-release model has proven useful in predicting the matrix-dependent contribution to the total tracer diffusion. The tracer motion from this mechanism consists of displacement of M-chain segments when P-chain self-diffusion removes a constraint. The constraint-release diffusion coefficient is given by[4]

$$D_{CR} = \alpha_{CR} D_0 M_e^2 M^{-1} P^{-3} \tag{3}$$

where the prefactor α_{CR} is defined by

$$\alpha_{CR} = \frac{48}{25} z \left(\frac{12}{\pi^2}\right)^{z-1} \tag{4}$$

and z is the "number of suitably situated constraints", a parameter presumed to be independent of M or P. The reptation and constraint-release motions are assumed to be independent, and therefore the tracer diffusion coefficient is predicted to be the sum of the two contributions, or

$$D^* = D_R + D_{CR} \tag{5}$$

This model has provided an accurate prediction of the M and P dependencies[6,7] of the diffusion of linear PS in PS melts.

Diffusion in Systems of Cyclic Polymers. The synthesis of monodispersed ring-shaped polymers[9-12] has stimulated investigations of the effects of polymer topology on polymer diffusion. One such study, which follows as a natural extension of the previous experiments on linear polymer systems, explores the effect of replacing either the matrix polymer or the tracer polymer with rings of equivalent molecular weight. Results for the diffusion coefficients of linear tracer molecules in ring matrices will be presented for the first time in this study. Conclusive evidence is shown that linear tracers diffuse at the same rate in a melt of rings as in a linear polymer melt, seemingly

0024-9297/92/2225-3942$03.00/0

in contradiction of any straightforward extrapolation of results from conventional models of matrix-dependent diffusion.

The diffusion of ring tracers into linear melts has already been studied by Mills et al.[13] with the conclusion that ring tracer chains diffuse more slowly in a matrix of linear chains than do linear tracer chains of the same molecular weight, in agreement with the concept introduced by Klein of ring threading or pinning by matrix chains.[14] Another tentative conclusion, namely, that for sufficiently high matrix molecular weights P the diffusion coefficient of a ring tracer will be P invariant, is confirmed. Preliminary results from the diffusion of the same tracer ring in ring melts show that ring matrices behave (for ring diffusion) similarly to linear matrices, as was noted for our experiment using linear tracers. Finally, an extreme dependence (D^* proportional to $M^{-4.5\pm0.2}$) of the ring diffusion coefficient with molecular weight was found in matrices of intramolecularly cross-linked polymers, a much higher dependence than was previously seen by Mills et al. for ring diffusion in linear melts. We can only speculate as to the origin of this phenomenon.

Experimental Section

Materials. Polystyrenes of three different molecular topologies were investigated in this study, including linear, cyclic[9-12] (or, "ring"-shaped), and the internally cross-linked "microgel",[15-17] all of which have been developed recently following advances in anionic polymerization techniques. The synthesis of the ring PS molecule proceeds after a linear precursor PS has been polymerized in a manner that leaves it bifunctionally anionic. The two "living ends" of the polymer are then allowed to react with dibromo-*p*-xylene, closing the ring. The reaction is carried out in a very dilute solution so that the probability of joining of two linear molecules is low. Fractionation removes any small amount of linear material (twice the ring molecular weight) formed in this manner. A good solvent is used so that the polymer is swollen, and the ring is therefore less likely to form in a knotted conformation. It is to be emphasized that these cyclic polymers are exactly the same as those whose tracer diffusion coefficients and small-angle neutron scattering characteristics are reported in refs 13 and 18, respectively. In ref 18 it is shown unequivocally that the polymers are rings and are essentially unknotted.

The molecular weight characterization of most of our ring samples was accomplished by wide-angle light scattering (WALS) and small-angle neutron scattering (SANS),[18] in addition to gel permeation chromatography (GPC). The weight-average molecular weight M_w determined by GPC was found to be a factor of 1.3 lower than that measured by the scattering methods, a result (due to the more compact conformations of rings than those of linear chains) that is consistent with similar measurements by others.[9] For ring samples not characterized by light scattering, GPC measurements were used (with the correction factor) to obtain M_w.

The intramolecularly cross-linked polymer, or microgel, is created by cross-linking a monodisperse precursor PS with *p*-bis(chloromethyl)benzene. The reaction is carried out in dilute solution, and subsequently a certain fraction of the cross-links occur between segments of the same polymer. Intermolecularly cross-linked material (of much higher molecular weight) is removed by fractionation. The average number of cross-links in the microgel is determined by ultraviolet spectrometry, and the molecular weight is measured by light scattering methods. From these two quantities and the circumstances of the cross-linking, the topology is inferred to consist of loops (possibly mesh) and dangling ends.

Sample Preparation. Bilayer film samples of d-PS and PS were prepared, using a silicon wafer as a physical support. Two different sample geometries were used in the study, either a thin tracer film of d-PS on a PS matrix or a thin tracer film of PS on a d-PS matrix. The choice of specimen geometry was determined by the availability of the d-ring and d-microgel materials. The tracer diffusion coefficient D^* of PS in d-PS or d-PS in PS was expected to be equivalent (for the same combination of molecular weights), since the molecular weights of the polystyrenes used were such that the effects of the small d-PS–PS interaction[19,20] were insignificant.

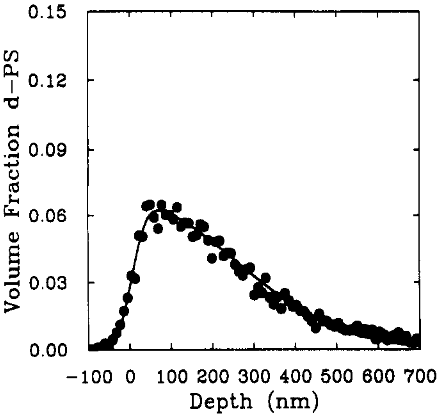

Figure 1. FRES spectrum from a bilayer sample composed of a 255 000 molecular weight linear d-PS tracer diffused in a 181 000 PS ring matrix. The sample had been annealed for 24 h at 150 °C. The solid line represents the convolution of the Gaussian system resolution function with eq 6. The tracer was 21 nm thick (found by integration), and the D^* value giving the best fit was 4.5×10^{-15} cm^2/s.

Matrix films of PS were prepared by drawing a silicon substrate at constant speed from a concentrated solution (5–10%, depending on molecular weight) of the matrix polystyrene in toluene, producing a film approximately 5 μm thick. Matrices of d-PS, necessarily about 400 nm thick in order to be useful in the FRES technique, were cast by spin-coating a d-PS/toluene solution on silicon. The tracer layer was prepared in a solventless transfer method. A solution of ca. 0.5 wt % tracer PS or d-PS in toluene was spun onto a glass slide at 2000 rpm and subsequently dried to form a film of thickness 20–50 nm. This film was released from the glass slide onto the surface of a water bath, from which it was picked up onto the surface of the matrix film and allowed to dry. The bilayer specimen was annealed at a temperature of 150 or 170 °C.

The concentration profile of the tracer molecules in the matrix was measured by forward recoil spectrometry (FRES), as has been described in previous publications.[21] Figure 1 shows a typical concentration profile from a bilayer of linear d-PS, molecular weight 255 000, and ring PS, molecular weight 181 000, after annealing for 24 h at 150 °C. The solid line represents the equation

$$\phi_{\text{tracer}} = 0.5\left[\operatorname{erf}\left(\frac{h-x}{w}\right) + \operatorname{erf}\left(\frac{h+x}{w}\right)\right] \qquad (6)$$

where $w = (4D^*t)^{0.5}$. The best fit of eq 6 to the data was obtained with a value of 4.5×10^{-15} cm^2/s for D^*, given the diffusion time t and the thickness of the tracer film h (taken to be the integral of the experimental data). The uncertainty in the diffusion coefficient per measurement is approximately 15%.

Results and Discussion

Diffusion of Linear Tracer Molecules in Ring Matrices. In the first study, the diffusion of linear d-PS tracer molecules was measured in linear and ring PS matrices. The results can be seen in parts a–c of Figure 2, which display the diffusion coefficients found for d-PS tracers of molecular weight M = 255 000, 520 000, and 915 000, respectively, in matrices of linear PS and PS rings, of molecular weight P ranging from 17 500 to 2×10^7. The data were collected in the manner described above, with the exception that, for M = 520 000 or 915 000 and P near 80 000, identical samples were compared after diffusion at either 150 or 178 °C to obtain a temperature conversion factor for the diffusion coefficient. Samples with M =

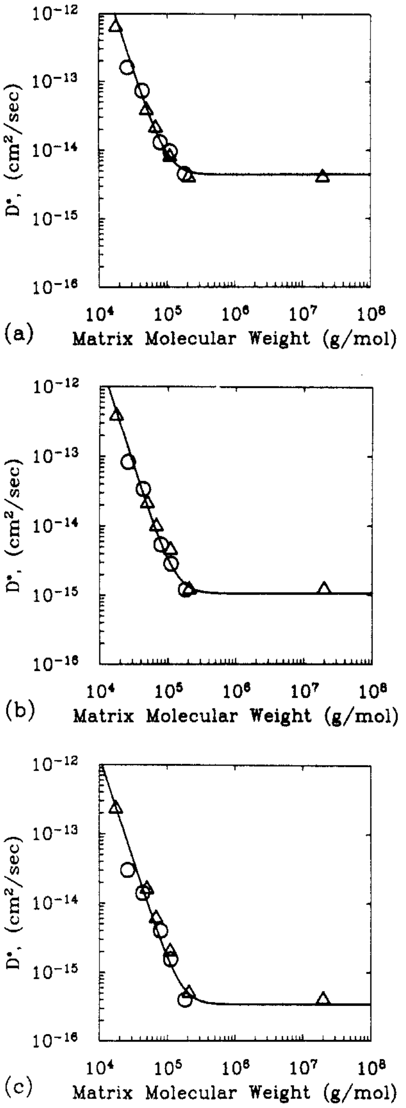

Figure 2. Diffusion coefficient of deuterated linear tracer molecules, molecular weight M, in PS matrices of molecular weight P. Triangles: linear PS matrices. Circles: ring PS matrices. Solid line: prediction of reptation and constraint release for linear chains. (a) $M = 255\,000$. (b) $M = 520\,000$. (c) $M = 915\,000$.

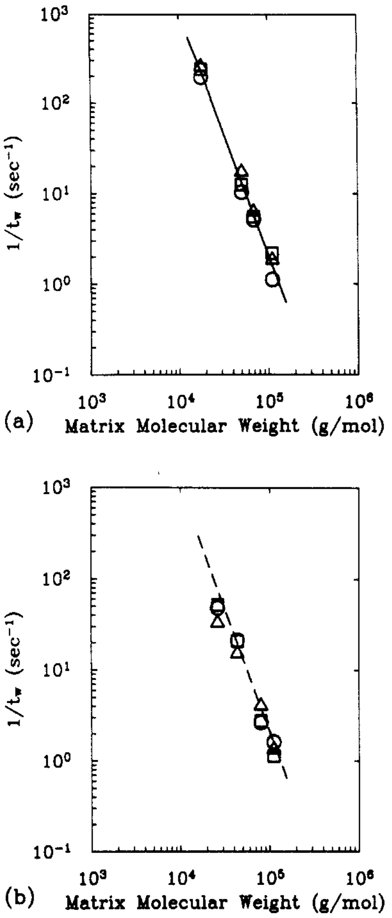

Figure 3. (a) Master curve of constraint-release waiting time (as computed by eq 8) vs matrix molecular weight of linear PS, for three different tracer molecular weights M. Circles: $M = 255\,000$. Squares: $M = 520\,000$. Triangles: $M = 915\,000$. Solid line represents best fit, with slope -2.7 ± 0.1. (b) Master curve of constraint-release waiting time (as computed by eq 8) vs matrix molecular weight of ring PS, for three different tracer molecular weights M. Circles: $M = 255\,000$. Squares: $M = 520\,000$. Triangles: $M = 915\,000$. Dashed line: best fit to linear PS matrices from Figure 3a.

520 000 or 915 000 and P greater than 80 000 were diffused at 178 °C, and the diffusion coefficients for these data points were scaled to 150 °C using the conversion factor.

The solid line in Figure 2 represents the diffusion coefficient given by eq 5. The value 2.85×10^{-4} was used for D_0, as obtained from the data using eq 1 and the diffusion coefficients measured in samples with the highest matrix molecular weights. A value of $z = 3.5$ appropriate to linear PS molecules was also used. For each tracer molecular weight, the ability of the constraint-release and reptation models to predict the data obtained with linear PS matrices is good, as noted earlier in reference to previous studies. Most significant, however, is the ability of the same equation to predict the data from the PS ring matrices as well, without adjustment of the parameters. As we shall discuss, the identical rate of diffusion for linear tracers in ring and linear matrices is a remarkable result for which no fully satisfactory explanation exists.

To assess the combined data of Figure 2, a single master curve can be generated by separating the diffusion contributed by the matrix and determining the "waiting time" t_w corresponding to the interval between the release of matrix constraints.[4] If D_R is the plateau D^* value for high P, then D_m, the matrix-dependent part of the diffusion, is given by

$$D_m = D^* - D_R \qquad (7)$$

The assumption implicit in eq 7, namely, that the tracer reptation and matrix contributions are independent, is justified since reptative motion is constrained by the matrix to follow the contour of the chain, whereas the motion due to constraint release is in general perpendicular to the chain contour. The waiting time can be written as

$$\frac{1}{t_w} = \frac{75}{4} D_m \frac{M}{K M_e^2} \qquad (8)$$

where

$$K = R^2/M \qquad (9)$$

and R is the end-to-end distance of the tracer polymer. The value of K (calculated from values[22,23] of the radius of gyration) is about 0.47 Å²/Da. Comparing eqs 3, 5, and 8, one can see that the waiting time should be independent of tracer molecular weight, thus allowing the different data sets of Figure 2 to be superposed.

Figure 3a shows the master curve formed by plotting t_w^{-1} against the matrix molecular weight P for the diffusion data measured in linear PS matrices. As one can see in the figure, the data sets from different tracer molecular weights do indeed superpose. A linear regression of log (t_w^{-1}) vs log (P), the result of which is shown as the solid line in the figure, shows that the waiting time scales as $P^{-2.7\pm0.1}$, a result in excellent agreement with previous measurements.[24] The power law dependence of t_w^{-1} on P is also in good agreement with eq 3, the constraint-release model according to Graessley. Figure 3b displays t_w^{-1} versus P for the data from ring matrices; once again the data sets from different molecular weights superpose. The dashed line in the figure shows the power law obtained from the linear matrices and matches the ring-matrix data extremely well.

The ability of eq 3 to model constraint-release-type diffusion in both linear and ring matrices is a curious result, since the equation was developed with the assumption that reptative motion could describe the self-diffusion of the matrix chains. Given the generally smaller diffusion coefficients for ring diffusion in linear matrices (at least for higher molecular weight rings), we might expect ring self-diffusion to be similarly slow, resulting in higher waiting times for constraint release. This line of reasoning is not supported by our data and also fails for diffusion involving polymers with star-type topologies.[25,26] The diffusion of linear molecules in matrices of star-shaped molecules is faster than the diffusion of linear chains in linear matrices and depends (at least for low arm molecular weights) less strongly on the matrix molecular weight. This result is surprising since star diffusion in linear matrices is slower than linear diffusion in the same matrices.

One feature of a ring matrix that might make it more amenable to theoretical description is the complete absence of chain ends. A recent treatment of Hess[27] of matrix-dependent diffusion (which correctly predicts the M and P dependencies of D_R), while not specifically treating the problem of ring matrices, does have the feature of being insensitive to matrix chain ends, and therefore one might test it against our data. The M and P dependencies of the matrix contribution to diffusion are predicted to scale according to the relation

$$D_m \sim M^{-1}P^{-1} \tag{10}$$

The tracer molecular weight dependence of D_m in eq 10 is correct, as our data show $D_m \sim M^{-1}$ for linear tracer diffusion in linear or ring matrices. The prediction that D_m should scale as the reciprocal of the matrix molecular weight is, however, very much at odds with the $P^{-2.7}$ dependence we find in both the ring and linear PS matrices, and therefore this model fails to describe our results.

Perhaps a key to the problem of the similarity of D_m in ring and linear matrices is associated with another similarity between ring and polymer melts, namely, in the value and molecular weight dependencies of η_0, the zero shear rate viscosity.[28] We do not, however, believe that the melt viscosity is the primary factor in D_m, as is sometimes suggested. For instance, one treatment[29] of the matrix contribution to tracer chain motion, superposed over reptative motion, assumes it to arise from the movement of the tracer coil through a homogeneous medium, according to the Einstein relation

$$D_m = k_B T/\zeta \tag{11}$$

where ζ is the mean matrix friction factor. Taking ζ to the proportional to the viscosity gives

$$D_m \sim \eta_0^{-1} \tag{12}$$

which would lead to the prediction that D_m should be equal in ring or linear matrices having the same η_0. However, in the melt it is found experimentally[28,30] that for high P values $\eta_0 \sim P^{3.4}$, and therefore the P dependence of eq 12 is in significant disagreement with our result $D_m \sim P^{-2.7}$. This discrepancy shows that the viscosity of the melt cannot by itself control D_m, though other factors may determine the properties of both.

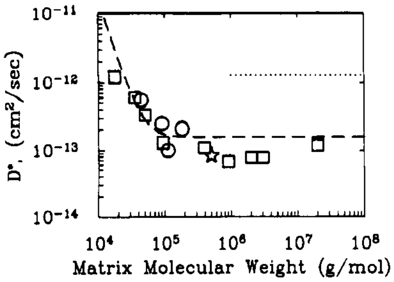

Figure 4. Diffusion coefficient of deuterated ring tracer molecules, M = 28 800, in PS matrices of molecular weight P. Squares: linear PS matrices. Circles: ring PS matrices. Star: microgel matrix and M = 26 000 PS ring tracer. Dashed line: prediction of reptation and constraint release for linear chains. Dotted line:the Rouse model.

Diffusion of Ring Tracer Molecules in Linear Matrices. In the second experiment, tracer diffusion of deuterated polystyrene rings (d-rings), molecular weight M = 28 800, was measured in a matrix of linear polystyrene, having a molecular weight P ranging from 17 500 to 2 × 10^7. The diffusion anneal was performed at 150 °C. The diffusion coefficient D^* of the d-ring tracer was measured as a function of the matrix molecular weight P, with the results displayed in Figure 4. The D^* values are seen to decrease with increasing P, reaching a lower limit of approximately 10^{-13} cm²/s for P greater than about 200 000. As noted before, previous studies[13] have indicated that ring tracers can reach a lower D^* limit for large enough P. Our data confirm this result, at least for a relatively low molecular weight ring tracer. Another feature of our data that is in agreement with the previous results (for approximately the same ring molecular weight) is the close match of the data to eq 5, the prediction for the diffusion coefficient of linear tracers in linear matrices (shown in the figure as the dashed line). This is in accordance with Klein's model,[14] for which a key factor limiting ring diffusion is the threading of the ring by linear matrix chains. For low molecular weight rings, however, the probability of threading is insigificant and the chain is allowed to undergo some form of reptative motion.

On the other hand, our results do not prove that rings diffuse by reptation, since other models provide for a matrix-independent diffusion coefficient. For instance, one could imagine the ring diffusing as a coil, with the diffusion coefficient given by the Einstein relation of eq 11. If one assumes that the friction factor can be approximated by the Rouse model,[31] then a tracer chain of N_m segments will be given by

$$D_{\text{Rouse}} = \frac{k_B T}{N_m \zeta_0} \tag{13}$$

This relation can be rewritten in terms of eq 2, or

$$D_{\text{Rouse}} = \frac{15}{4}\frac{D_0}{M M_e} \tag{14}$$

Taking M_e and D_0 for the ring to be the same as those of linear chains, we get a value of 1.3×10^{-12} for D_{Rouse}, which is about an order of magnitude too high, as seen in Figure 4. Another clear disadvantage of the Rouse model is its inability to describe the rise in D^* with decreasing P values below $P = 10^5$.

Figure 4 also shows the diffusion coefficients obtained for d-PS ring diffusion in PS ring matrices of molecular

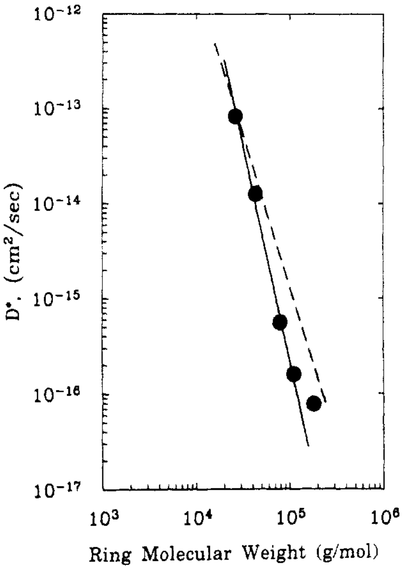

Figure 5. Diffusion coefficient of ring tracer molecules, of molecular weight *M*, in deuterated microgel PS matrices of molecular weight 490 000. The dashed line shows the $M^{-3.2}$ dependence found by Mills et al. for the diffusion coefficient of rings in very high molecular weight linear matrices. The solid line is a fit to lower *M* values, with slope −4.5 ± 0.2.

weight *P*. The results lay in the region for which D^* depends on *P*, and it is therefore quite noteworthy that the diffusion coefficients are close to those for d-PS ring diffusion in linear matrices. This result, another example of the similarity of tracer diffusion in linear and ring matrices noted in the previous section, does not, unfortunately, allow us to decide between the various models for ring diffusion mentioned above. On the other hand, were this experiment to be performed again with high d-ring molecular weights (unavailable at the moment), the threading or pinning of a ring tracer chain by ring matrix chains should come into effect. One might expect threading to occur with a lower probability for ring matrix chains than for linear matrix chains. Therefore, following Klein's model for ring reptation, ring diffusion would be faster in rings than in linear matrices, and we would expect to see a noticeable difference between results from the two matrix topologies.

Diffusion of Ring Tracer Molecules in Microgel Matrices. Our final experiment was a study of ring diffusion in a matrix with yet another topology, this being the intramolecularly cross-linked PS "microgel". The diffusion coefficient D^* of PS rings in a 490 000 molecular weight d-microgel (with an average of 20 monomers between cross-links) melt was measured as a function of the molecular weight *M* of the ring tracer molecule, resulting in the data displayed in Figure 5. The D^* data show an extremely strong dependence on *M*, decreasing as $M^{-4.5\pm0.2}$ for the lower values of *M*. This dependence is much greater than the $M^{-3.2}$ power law found by Mills et al. for ring diffusion in high molecular weight linear matrices (displayed in the figure as the dashed line) or the M^{-2} dependence found for the diffusion of linear chains in microgel matrices.[32]

On the other hand, the diffusion coefficient for the 26 000 molecular weight ring in the microgel is close to the high molecular weight plateau value found for the 28 800 d-ring diffusion coefficient in linear chains, as shown in Figure 4. The drastic *M* dependence must therefore take place for *M* above 30 000. It is possible that for these larger *M* values the hindrance of ring diffusion might occur in analogy with Klein's model for ring diffusion in linear melts, i.e., pinning of the ring by dangling ends or loops of the microgel matrix molecules.

In one last attempt to assess the microgel data, we refer to another theory for ring tracer diffusion which may be applicable to this experiment. Rubinstein[33] has used a lattice model to calculate the dynamics of a closed random walk. Such a model has its closest real analogy to a ring polymer diffusing in a cross-linked network, or gel. One result of Rubinstein's theory is the scaling relation $D^* \sim M^{-2}$. This power law clearly does not compare favorably with our result $D^* \sim M^{-4.5\pm0.2}$ for ring diffusion in microgels. Once again the difference may be the loops or dangling ends of the microgel which do not appear in the lattice model.

It may seem contradictory that as matrices rings provide the same constraint release as linear chains but as tracers rings and linear chains diffuse very differently into linear[13] and microgel matrices. Rings are not the only chain topology for which this apparent tracer/matrix contradiction appears; polystyrene stars with arms of molecular weight M_a several times M_e diffuse as tracers very slowly into high molecular weight linear matrices[16,25] whereas their behavior as matrices is quite similar when compared to matrices of linear chains with molecular weight comparable to the star "span" of $2M_a$.[25,26] Apparently both rings and stars of modest molecular weight can diffuse cooperatively when they make up the majority of the matrix in such a way that their dynamics are not much different from that of linear chain matrices.

Conclusions

Diffusion was studied for PS molecules of three different topologies, linear, ring, and microgels. The diffusion coefficients of deuterated linear chains in ring matrices were found to be nearly identical to those in linear matrices, implying that entanglements form and disappear with the same rate in matrices of these two topologies. No theory was found to predict this behavior, although the closeness of the melt viscosities for ring and linear chains lends support to the idea of similar dynamics for these topologies.

The first unambiguous data showing a high molecular weight plateau in the diffusion coefficient D^* of ring tracer molecules (28 800 molecular weight) in linear PS was presented, supporting, but not proving, the hypothesis that ring-shaped molecules can undergo a form of reptation. The diffusion coefficients were very close to those expected for linear tracer chains of the same molecular weight. Preliminary data for the diffusion of d-rings into ring matrices were found to be diffusion coefficients very close to those in linear matrices of the same *P* value. The diffusion of rings of various molecular weights *M* into microgel matrices was found to obey the power law $M^{-4.5\pm0.2}$ for lower *M* values. This molecular weight dependence is even higher than that found by Mills et al. for ring diffusion in linear chains. Again, no theory could be advanced to account for this behavior, other than the idea of chain hindrance upon threading of the ring by matrix chains, as developed for linear matrices by Klein.

Acknowledgment. We are indebted to P. Rempp and A. Kovacs of Centre de Research de Macromolecules, CNRS, Strasbourg, France, for their contributions to the preparation of ring polystyrenes. We also acknowledge support of this study by the National Science Foundation and are grateful for the use of the facilities of the Materials Science Center, Cornell University, which is funded by the DMR-MRL program of the NSF.

References and Notes

(1) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.

(2) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; p 222.
(3) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789.
(4) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(5) Graessley, W. W. *Faraday Symp. Chem. Soc.* **1983**, *18*, 7.
(6) Green, P. F.; Mills, P. J.; Palmstrøm, C. J.; Mayer, J. W.; Kramer, E. J. *Phys. Rev. Lett.* **1984**, *53*, 2145.
(7) Green, P. F.; Kramer, E. J. *Macromolecules* **1986**, *19*, 1108.
(8) Tead, S. F.; Kramer, E. J. *Macromolecules* **1988**, *21*, 1513.
(9) Hild, G.; Kohler, A.; Rempp, P. *Eur. Polym. J.* **1980**, *16*, 525.
(10) Hild, G.; Strazielle, C.; Rempp, P. *Eur. Polym. J.* **1983**, *19*, 721.
(11) McKenna, G. B.; Hadziioannou, G.; Lutz, P.; Hild, G.; Strazielle, C.; Rempp, P.; Kovacs, A. *Macromolecules* **1987**, *20*, 498.
(12) Lutz, P.; Strazielle, C.; Rempp, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27* (1), 190.
(13) Mills, P. J.; Mayer, J. W.; Hadziioannou, G.; Lutz, P.; Strazielle, C.; Rempp, P.; Kovacs, A. J.; Kramer, E. J. *Macromolecules* **1987**, *20*, 513.
(14) Klein, J. *Macromolecules* **1986**, *19*, 105.
(15) Antonietti, M.; Sillescu, H.; Schmidt, M.; Schuch, H. *Macromolecules* **1988**, *21*, 736.
(16) Antonietti, M.; Sillescu, H. *Macromolecules* **1986**, *19*, 798.
(17) Antonietti, M.; Sillescu, H. *Macromolecules* **1985**, *18*, 1162.
(18) Hadziioannou, G.; Cotts, P. M.; ten Brinke, G.; Han, C. C.; Lutz, P.; Strazielle, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 439.
(19) Bates, F. S.; Wignall, G. D.; Koehler, W. C. *Phys. Rev. Lett.* **1985**, *55*, 2425.
(20) Bates, F. S.; Wignall, G. D. *Phys. Rev. Lett.* **1986**, *57*, 1429.
(21) Mills, P. J.; Green, P. F.; Palmstrøm, C. J.; Mayer, J. W.; Kramer, E. J. *Appl. Phys. Lett.* **1984**, *45*, 957.
(22) Benoit, H.; Cotton, J. P.; Decker, D.; Farnoux, B.; Higgins, J. S.; Jannink, G.; Ober, R.; Picot, C. *Nature (London)* **1973**, *245*, 13.
(23) Wignall, G. D.; Ballard, D. G.; Schelten, J. *Eur. Polym. J.* **1974**, *10*, 861.
(24) Green, P. F. Ion Beam Analysis of Diffusion in Polymer Melts. Ph.D. Dissertation, Cornell University, 1985; University Microfilms, Inc.: Ann Arbor, 1985; Chapter 5.
(25) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Antonietti, M.; Sillescu, H. *Macromolecules* **1988**, *21*, 2578.
(26) Shull, K. R.; Dai, K. H.; Kramer, E. J.; Fetters, L. J.; Antonietti, M.; Sillescu, H. *Macromolecules* **1991**, *24*, 505.
(27) Hess, W. *Macromolecules* **1987**, *20*, 2587.
(28) Roovers, J. *Macromolecules* **1985**, *18*, 1361.
(29) Daoud, M.; de Gennes, P.-G. *J. Polym. Sci., Polym. Phys.* **1979**, *17*, 1971.
(30) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(31) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(32) Antonietti, M.; Sillescu, H. *Macromolecules* **1986**, *19*, 793.
(33) Rubinstein, M. *Phys. Rev. Lett.* **1986**, *57*, 3025.

Registry No. PS (homopolymer), 9003-53-6; S/*p*-bis(chloromethyl)benzene (copolymer), 30446-12-9.